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TITLE: PREDICTION AND SYNTHESIS EFFORTS AT LOS ALAMOS

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One important aspect of an organic synthesis effort related to the
development of new explosives, is the ability to estimate the properties of
proposed molecules. Accurate predictions of the properties of these
molecules can help target those molecules that might prove better than
existing explosives. Novel explosives are being proposed, at Los Alamos and
elsewhere, that are qualitatively different in their molecular makeup than
most of the existing conventional ones. These explosives include, highly
strained cage molecules, heterocyclic molecules, low hydrogen-containing
molecules, and high nitrogen-containing molecules.

In most cases, the detonation velocity and C-J pressure are estimated
for the proposed explosive using any number of existing predictive methods.
These include the BKW code[1,2], the TIGER code[3], the empirical methods of
Kamlet and Jacobs[4], and of Rothstein and Petersen[5,6]. The first two methods
solve the hydrodynamic-thermodynamic equations subject to an assumed form
for the equations-of-state of the products. It should be noted that,
although these two codes are similar in principle, they can yield very
different results. For example, the TIGER code, which allows for the
formation of formic acid as a detonation product, predicts very different
products for HMX than does the BKW code (see Table I.). These equations-of-
state are usually obtained by parametric adjustments so as to reproduce
performance data on well-characterized explosives. The method of Kamlet and

Jacobs is a parametric fit to data produced by the RUBY code[7] - a precursor to the TIGER code. The last method fits experimental detonation velocity data with parameters related to the structure of the molecule. The organic chemist then decides, based on these results, if the proposed compound should be made.

Recently some new organic explosives were synthesized at Los Alamos[8] that were somewhat different from the majority of the explosives that presently exist. The above predictive methods were used to estimate the detonation velocity and C-J pressure of these new compounds, and it was found that the predicted values differed significantly from the preliminary measured perforamance data. These results led to a re-examination of these methods and their reliability for guiding a synthetic organic effort. It appears that, because all of these methods contain adjustable parameters in their actual implementation, that there is just too little experimental performance data (on pure explosives) on which to judge the merits of these methods for compounds that are qualitatively different from those on which the method was parameterized. The rest of this paper will be concerned with alternate ways of viewing detonation velocities and a new method for estimating the detonation velocity of a proposed compound. The main advantage of this new method lies in its simplicity as it allows one to determine the most important aspects of a proposed molecule that contribute to its performance.

Although various performance characteristics are important in deciding if a particular compound will prove useful for a particular application, we will be concerned here with only the detonation velocity. The detonation velocity is the most accurately and directly measured quantity related to

performance and, indeed, other performance characteristics like C-J pressure, are dependent on the detonation velocity.

Our first objective is to examine the available detonation velocity data on pure explosives in a way that allows one to perhaps identify other molecules that have high detonation velocities. We will deal here only with carbon-, hydrogen-, nitrogen-, and oxygen-containing explosives.

We will assume that the detonation velocity of an explosive is a function of its atomic composition $(C_aH_bN_cO_d)$, heat of formation (ΔH_f^o), and density (ρ). For example, RDX $(C_3H_6N_6O_6)$ and HMX $(C_4H_8N_8O_8)$ are observed to have the same detonation velocity if HMX is pressed to the same density as RDX. These two explosives have the same proportions of carbon, hydrogen, nitrogen, and oxygen and also have about the same relative heat of formation (14.7 kcal/mole for RDX and 17.9 kcal/mole for HMX). Thus it would seem that one could "normalize" the molecular formula such that $a+b+c+d=1$. This being the case, we can take advantage of a property of a regular tetrahedron to systematically locate all the known explosives. A regular tetrahedron has the property that the sum of the four perpendicular distances from any interior point to the four sides is a constant, which we can arbitrarily take to be unity. Thus, if we identify the four corners as representing carbon, hydrogen, nitrogen, and oxygen, then any interior point will represent any CHNO compound whose molecular formula has been normalized That is the four elements have coordinates given by:

Nitrogen: (0, 0, 3/4)

Oxygen: (√2/2 0, 1/4)

Carbon: (-√2/2, √6/4, -1/4)

Hydrogen: (√2/4, -√6/4, -1/4).

This is a tetrahedron centered at the origin and where the four distances from any interior point to each of the four sides sum to unity. The following formulas can be used to locate any organic compound in this tetrahedron:

$$x = \sqrt{2}(3D - 1 + C)/4 \qquad\qquad \text{Eq. 1}$$

$$y = \sqrt{6}(A - B)/4$$

$$z = C - 1/4$$

where $A=a/n$, $B=b/n$, $C=c/n$, $D=d/n$, and $n=a+b+c+d$.

One concept of interest in explosives is that of oxygen balance. This is related to the amount of oxygen needed to burn all of the carbon and hydrogen to their most stable products. Usually these products are taken to be carbon dioxide and water, and will be the ones selected here. These two products along with nitrogen gas then define three points in the tetrahedron space, which in turn define an "oxygen balance" plane. It would seem reasonable then to define the oxygen balance of any compound as the perpendicular distance from its position in the tetrahedron space to this oxygen-balance plane. The formula for this definition of oxygen balance is given by.

$$OB = \frac{d - 2a - b/2}{5(a+b+c+d)} \qquad\qquad \text{Eq. 2}$$

This differs from the more common definition of oxygen balance[9] given by

$$OB = \frac{d - 2a - b/2}{M} \qquad\qquad \text{Eq. 4}$$

where M is the molecular weight of the compound. Although oxygen-balance does not play a major role in the theory to be presented below, it does provide a convienent reference plane

Figure 1 shows a stereo diagram of this tetrahedron, the positions of some common pure explosives and the oxygen-balance plane. This diagram points out that there are large regions of composition space that are devoid of any existing explosives, and that there are regions (large nitrogen content, for example) that may prove to contain higher performing molecules than HMX. It is interesting to note that most of these explosives are clustered around TNT and the others are all relatively close to the oxygen balance plane.

We now examine a method originally proposed by Urizar[10] at Los Alamos during the late 1940's for predicting the detonation velocity for mixtures. Here we will attempt to modify this method to make it applicable to pure explosives and hence so it can be used as a predictive method. The basic idea is to assume that the performance (detonation velocity here) of a mixture of known well-characterized explosives with a particular atomic composition, heat of formation, and density is the same as that of a pure compound having the same atomic composition, heat of formation, and density

Urizar's method assumes that the detonation velocity of a mixture is the sum of the detonation velocities of the components weighted by their volume fractions. Although his method includes "charateristic transmission velocities" for nonexplosives (binders, inerts, additives, and voids) we will be concerned only with mixtures of explosives and voids He has determined the characteristic velocity of a void to be 1.5 km/s   Assuming his method to be valid and assuming that the detonation velocity of a mixture and a pure compound are the same if the compositions, heats of formations, and densities are the same, then it should be possible to concoct a mixture of five well-characterized explosives that matches the

atomic composition (a, b, c, and d) and heat of formation of the desired new explosive. Once the moles of each component are calculated it is an easy matter to use Urizar's method to estimate the detonation velocity of this mixture (along with some voids to attain the desired density of the new explosive).

As an example, we have chosen the five known explosives, BTNEU, RDX, TNETB, ABH, and ExplD as a "basis set" of well-characterized explosives with measured detonation velocities and densities. To test this method we can select any other known explosive with an observed detonation velocity and density, and use the described method to calculate its detonation velocity. The results are given in Table IV.

Viewed in another way, the above method yields a form for the predicted detonation velocity, D, of

$$D = D_0 + \rho \ (\alpha \ a \ + \beta \ b \ + \gamma \ c \ + \delta \ d \ + \ h \ \Delta H_f) \ M \qquad \text{Eq. 4}$$

where ρ is the density, M is the molecular weight and ΔH_f is the heat of formation of the proposed compound and $D_{.}$ is the transmission velocity of the voids. We can now fit, in a least-squares sense, observed detonation velocities using the six parameters α, β, γ, δ, h, and D_0. The results, using the data from Table III are.

$$\alpha = -13.85, \qquad \beta = 3.95, \qquad \gamma = 1.14$$
$$\delta = 68.11, \qquad D_0 = 1.69, \qquad h = 0.601$$

The detonation velocities for these explosives calculated using the above formula and parameters are listed in Table IV. Figure 2 shows a graphical comparison of the observed and calculated detonation velocities.

This formula points out that both hydrogen and nitrogen (relative to carbon) contribute to an explosive having a high detonation velocity, and in fact, carbon contributes negatively (α is negative) to the detonation velocity. This result is consistent with HMX being one of the best performing explosives and also one of the few that has significantly more hydrogen and nitrogen than carbon. However, it is also known that hydrogen results in compounds with low density (nitrogen on the other hand usually results in dense compounds) and hence trade-offs will have to be made between composition, heat of formation, and density in proposing new molecules that will out-perform our best existing explosives

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Table I. Detonation Products Predicted for HMX

Product	BKW (moles)	TIGER (moles)
H_2O	4.000	2.385
H_2	0.000	0.005
CO_2	1.996	1.382
CO	0.008	0.038
NH_3	0.000	0.135
N_2	4.000	3.933
HCOOH	.....	1.406
Solid C	1.996	1.175

Table II. Some common explosives and their formulas

	Acronym	C	H	N	O	Chemical Name
1	ABH	24	6	14	24	Azo bis(hexanitro) biphenyl
2	BTF	6	0	6	6	Benzotrifuroxan
3	BTNEU	5	6	8	13	bis(trinitroethyl) urea
4	DATB	6	5	5	6	Diamino-trinitrobenzene
5	DINA	4	8	4	8	Diethanolnitramine dinitrate
6	DIPAM	12	6	8	12	Dipicramide
7	ExplD	6	6	4	7	Ammonium picrate
8	HMX	4	8	8	8	Cyclo tetramethylene tetranitramine
9	HNAB	12	4	8	12	Bis(trinitrophenyl) diazine
10	HNS	14	6	6	12	Hexanitro stilbene
11	NG	3	5	3	9	Nitroglycerine
12	NONA	18	5	9	18	Nonanitroterphenyl
13	NQ	1	4	4	2	Nitroguanidine
14	ONT	18	6	8	16	Octanitroterphenyl
15	PETN	5	8	4	12	Pentaerythritol tetranitrate
16	Picric	6	3	3	7	Trinitrophenol
17	RDX	3	6	6	6	Cyclo trimethylene trinitramine
18	TACOT	12	4	8	8	Tetranitrobenzotriazolobenzotriazole
19	TATB	6	6	6	6	Triamino Trinitrobenzene
20	Tetryl	7	5	5	8	N-methyl-N,2,4,6-tetranitroaniline
21	TNA	6	4	4	6	Trinitroaniline
22	TNETB	6	6	6	14	Trinitroethyltrinitro butyrate
23	TNT	7	5	3	6	Trinitrotoluene

Table III. Detonation Velocities of the Compounds Listed in Table II.

Acronym	ρ_{TMD} g/cm^3	ΔH_f kcal/mole	ρ g/cm^3	D km/s
ABH	1.780	116.3	1.78	7.600
BTF	1.901	144.5	1.86	8.490
BTNEU	1.861	-72.9	1.86	9.01
DATB	1.837	-23.6	1.79	7.520
DINA	1.670	-75.4	1.60	7.720
DIPAM	1.790	-6.8	1.76	7.400
ExplD	1.717	-94.0	1.55	6.850
HMX	1.905	17.9	1.89	9.116
HNAB	1.799	67.9	1.60	7.311
HNS	1.740	18.7	1.70	7.000
NG	1.596	-88.6	1.600	7.700
NONA	1.780	27 4	1.78	7.560
NQ	1.775	-22.1	1.550	7.650
ONT	1.800	19.7	1.800	7.330
PETN	1.780	-128.7	1.760	8.260
Picric	1.760	-51.3	1.710	7.260
RDX	1.806	14.7	1.770	8.700
TACOT	1.850	110.5	1.850	7.250
TATB	1.938	-36.8	1.880	7.760
Tetryl	1.730	4.7	1.710	7.850
TNA	1.760	-29.9	1.72	7.300
TNETB	1.783	-118.5	1.78	8.460
TNT	1.654	-16.0	1.609	6.908

Table IV. Comparison of Observed and Calculated Detonation Velo-
cities

Acronym	D	$D^{\dagger}_{calc}$	$D^{\ddagger}_{calc}$
	km/s	km/s	km/s
ABH	7.600	(7.60)	7.63
BTF	8.490	8.34	8.51
BTNEU	9.01	(9.01)	8.95
DATB	7.520	7.74	7.51
DINA	7.720	7.71	7.83
DIPAM	7.400	7.54	7.46
ExplD	6.850	(6.85)	6.86
HMX	9.11	9.18	9.03
HNAB	7.311	7.05	7.29
HNS	7.000	7.02	7.04
NG	7.700	. . . .	. . . .
NONA	7.560	7.50	7.49
NQ	7.650	7.86	7.78
ONT	7.330	7.38	7.29
PETN	8.260	8.38	8.38
Picric	7.260	7.33	7.30
RDX	8.700	(8.70)	8.70
TACOT	7.250	7.55	7.38
TATB	7.760	8.13	7.70
Tetryl	7.850	7.58	7.62
TNA	7.300	7.36	7.25
TNETB	8.460	(8.46)	8.48
TNT	6.908	6.73	6.77

[†]Calculated using detonation data for the five explosives, ABH,
BTNEU, ExplD, RDX, and TNETB.

[‡]Calculated using Equation 4 and parameters determined from least
squares fit to detonation velocity data.

FIGURE CAPTIONS

Figure 1. Stereo plot in the tetrahedron space of the explosives listed in Table II. Figure 1b is an expanded view of Figure 1a.

Figure 2. Comparison of the experimental and calculated detonation velocities for the explosives listed in Table II. The calculated values were obtained using Eq. 4.
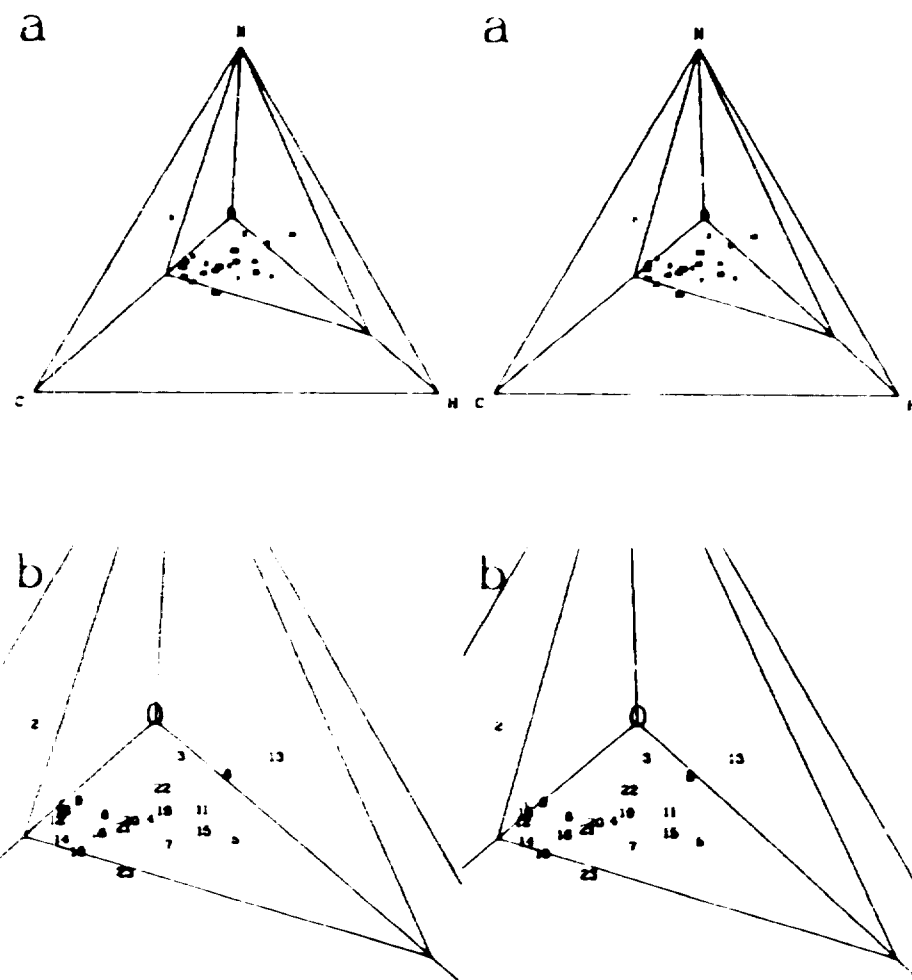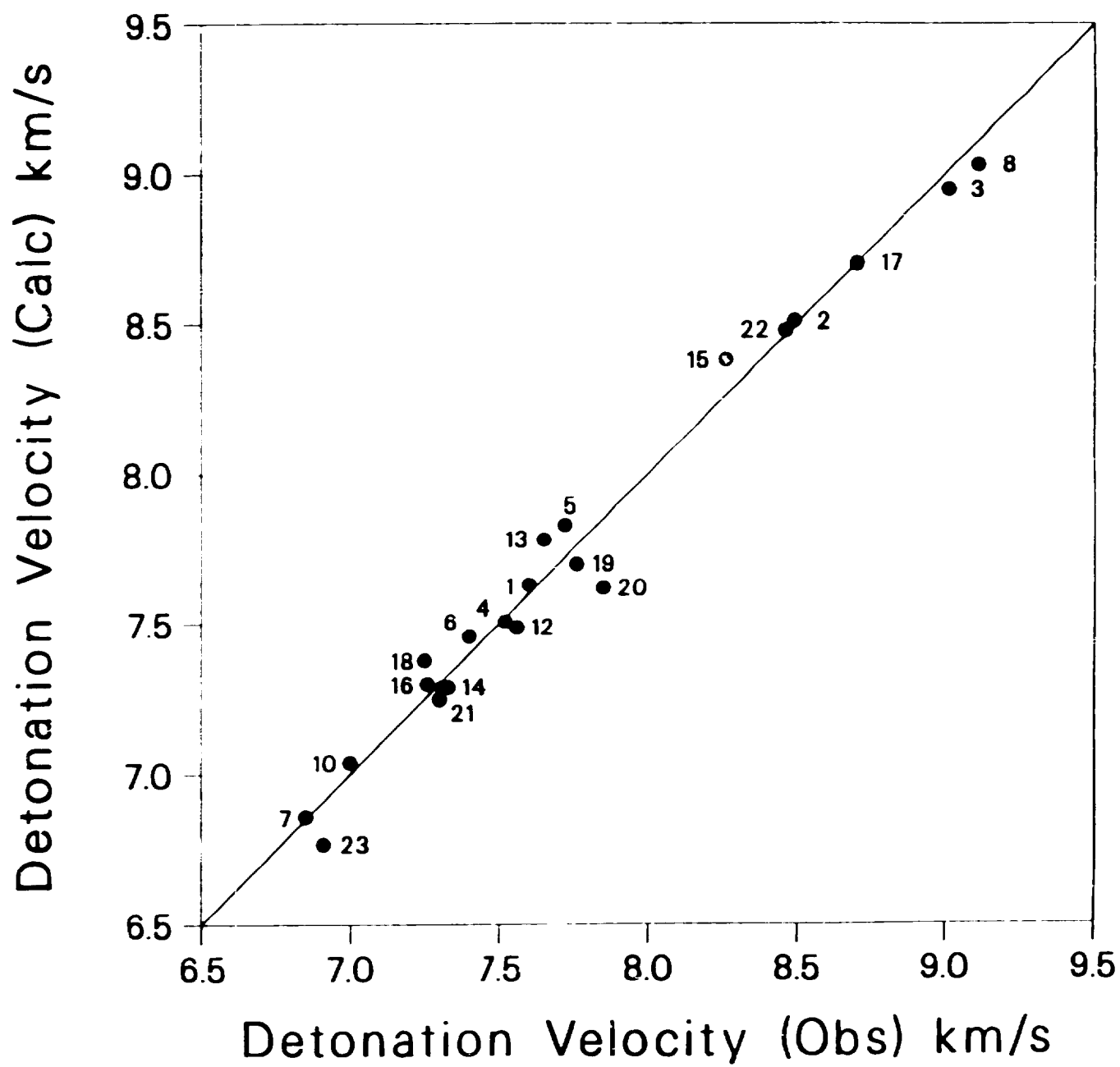
Figure 1

Figure 2